

Tutorial: Delayed Coking Fundamentals

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ABSTRACT

Great Lakes Carbon Corporation has worked closely with refineries producing delayed coke in all forms, fuel grade (shot or sponge), anode grade (sponge), and electrode grade (needle) since start-up of the company's first calcining operation in 1937. With on-going research in the area of delayed coking since 1942, Great Lakes Carbon (GLC) has operated delayed coking pilot units including an excellent large-scale pilot unit with a coke drum 0.3 meter (1 ft) diameter by 2.1 meters (7 ft) long and has developed physical models which explain coke formation in coke drums.

Knowledge of commercial delayed coking units as well as that of the GLC Pilot Delayed Coker is used in this tutorial paper to describe the formation and uses of the three types of structures of delayed petroleum coke: needle, sponge, and shot. Troubleshooting tips are included on many aspects of the delayed coking drum cycle including: steam stripping, water quenching, coke cutting, drum warm-up, and drum switching technique. Suggestions and descriptions of delayed coking unit hardware are included.

The objective of this tutorial paper is to acquaint the non-refinery technologist and further the knowledge of refinery personnel with the delayed coking operation, delayed coking unit hardware, types of coke that can be produced, coke formation models, and the uses of petroleum coke. Also, by discussing some of the delayed coking process problems encountered in the industry, we hope to encourage new advances, solutions, and improvements for the future.

WHAT IS DELAYED COKING?

Delayed coking is a thermal cracking process used in petroleum refineries to upgrade and convert petroleum residuum (bottoms from atmospheric and vacuum distillation of crude oil) into liquid and gas product streams leaving behind a solid concentrated carbon material, petroleum coke. A fired heater with horizontal tubes is used in the process to reach thermal cracking temperatures of 485 to 505°C (905 to 941°F). With short residence time in the furnace tubes, coking of the feed material is thereby “delayed” until it reaches large coking drums downstream of the heater. Three physical structures of petroleum coke: shot, sponge, or needle coke can be produced by delayed coking. These physical structures and chemical properties of the petroleum coke determine the end use of the material which can be burned as fuel, calcined for use in the aluminum, chemical, or steel industries, or gasified to produce steam, electricity, or gas feedstocks for the petrochemicals industry.

CRUDE OIL REFINING: WHERE DOES DELAYED COKING FIT IN?

To understand the delayed coking process, one must understand how the delayed coker is integrated with the rest of the refinery. Delayed coker feed originates from the crude oil supplied to the refinery. Therefore, brief descriptions of each of the processing steps preceding the delayed coking unit are provided below. A basic refinery flow diagram is shown on the following page in Figure 1.

Crude Oil Desalting

Crude oil contains around 0.2% water in which is mixed soluble salts such as sodium chloride and other metals which are on the edge of the sphere of water. In desalting, crude oil is washed with around 5% water to remove the salts and dirt from the crude oil. The water, being heavier than the oil, drops out of the bottom, and the cleaned oil flows overhead with around 0.1% water.

Atmospheric Distillation

The desalted crude oil is heated in a tube furnace to over 385°C (725°F), just below the temperature that cracking of the oil can occur, then flashed into a distillation column. The primary products are straight run gasoline, kerosene, jet fuel, diesel, atmospheric gas oil (AGO) and atmospheric reduced crude.

Vacuum Distillation

The atmospheric reduced crude (ARC) is then heated to around 395°C (743°F) and flashed into a vacuum distillation column that is operated at low pressures, 10 mm Hg absolute desired but more common 25 to 100 mm Hg absolute. The desired aim is to lift the maximum amount of oil boiling below 565°C into heavy vacuum gas oil (HVGO) reducing the production of vacuum reduced crude (VRC), the main feedstock to the delayed coker. The HVGO and the AGO are the principal feedstocks to a fluid catalytic cracking unit (FCCU) for the production of gasoline and diesel. Improving vacuum distillation is one of the best methods for increasing gas oil yield in a refinery while at the same time reducing the amount of vacuum reduced crude (coker feed). This enables higher refinery throughput rates to be achieved.

Crude Oil Storage

Desalter

Tube Furnace

Gasoline

Diesel

Fluid Cat. Cracker

Atm. Distillation

HGO

Vacuum Distillation

Coker Fractionator

Switch Valve

Tube Furnace

Delayed Coke Drums

Great Lakes Carbon Corporation

of these units were still in operation after World War II. Operators assigned as decokers used picks, shovels, and wheelbarrows and had rags wrapped around their heads to protect against the heat.

The coke that was produced in the horizontal stills had a high density, low volatile matter (VM) content of around 8 wt%, and less than 1 wt% moisture. One problem was that ash content was high, around 1 wt% compared to under 0.2 wt% in most modern delayed cokers. Connors [1] thought that this was due to the lack of desalting and washing of the crude oils processed at that time.

The origin of the vertical coke drum was probably from thermal cracking of gas oil for the production of gasoline and diesel fuel. From 1912 to 1935 the Burton process developed by Standard Oil at Whiting, Indiana converted gas oil to gasoline with the production of petroleum coke. Dubbs and other thermal cracking processes also produced petroleum coke. Lack of an adequate supply of crude oil and the lack of a heavy oil market caused land-locked middle American refineries to process the heavy fuel oil (atmospheric distillation bottoms and vacuum distillation bottoms) in a delayed coker to produce more gasoline and diesel fuel. Decoking the drums was difficult. "Manual decoking was a hot and dirty job. ...various mechanical devices were tried. One of the common systems employed was to wind several thousand feet of steel cable on holding devices in the drum. The cable was pulled by a winch, to loosen the coke. Coke was also removed by drilling a small hole, then a large hole, after which beater balls on a rotating stem knocked out the remaining coke [1]."

The first delayed coker was built by Standard Oil of Indiana at Whiting, Indiana in 1929 [2,3]. The development of hydraulic decoking came in the late 1930's. Shell Oil at Wood River, Illinois presented a paper on hydraulic decoking 4.0 m (13 ft) diameter Dubbs units and stated that they had patents along with Worthington Pump Company on hydraulic decoking bits and nozzles [4]. Standard Oil of Indiana had patents on the original cutting nozzles used by Pacific Pump [5]. A very similar nozzle is currently used in the new compact combination coke cutting unit. A pilot hole is drilled down through the coke in the drum using high pressure water, and then the coke is cut out with a drilling bit with horizontal water nozzles. Roy Diwok while at Standard Oil Whiting was one of the key people in developing the hydraulic decoking in the 1930's. Diwok in May 1952, while Executive Vice President of Pan Am Southern Corp. (Owned by Standard Oil of Indiana), worked with Great Lakes Carbon Corporation to produce the first needle coke in a delayed coker. Bernard Gamson, the Director of Research and Development for Great Lakes Carbon at the time, stated in a report that Diwok was "the father of delayed coking [3]."

Delayed coking combined a number of the features and improvements from the development of the thermal cracking process. The use of pressure as well as heat for cracking and separating the heater from the coker and the use of two drums enabled the delayed coker to operate on a continuous basis. The number of cokers built before 1955 was small, with a surge in delayed coker construction between 1955 to 1975 at 6% per year and an 11% growth rate during the 1965 to 1970 period [1]. The growth of delayed cokers was in step with the growth of fluid catalytic cracking and rapid decline in thermal cracking. A fluid coker, similar to a fluid catalytic cracker except that fluid coke is circulated instead of catalyst, was first built in 1954 at Billings, Montana. Five more fluid cokers were built in the late fifties, and one in 1970. In 1958, the head of petroleum refining engineering at Colorado School of Mines, J.O. Ball, stated that there would not be any more delayed cokers built. Ball thought all new cokers would be fluid cokers, and that a delayed coker was just a garbage can in the refinery. Today there are 49 operating delayed cokers in the U.S. and only six fluid cokers / flexicokers.

MODERN DELAYED COKING PROCESS

The delayed coker is the only main process in a modern petroleum refinery that is a batch-continuous process. The flow through the tube furnace is continuous. The feed stream is switched between two drums. One drum is on-line filling with coke while the other drum is being steam-stripped, cooled, decoked, pressure checked, and warmed up. The overhead vapors from the coke drums flow to a fractionator, usually called a combination tower. This fractionator tower has a reservoir in the bottom where the fresh feed is combined with condensed product vapors (recycle) to make up the feed to the coker heater.

Delayed Coking Drum Cycle

Since the feed stream is regularly switched between drums, a cycle of events will occur on a regular interval depending on the delayed coking unit feed rate, drum size, and throughput capacity. Most typical delayed cokers currently run drum cycle times of about 16 hours with one drum filling on-line while its counterpart is off-line for stripping, cooling, and decoking. Drum cycle event approximate time requirements for such a cycle are shown below in Table 1. Shortening the cycle time is one method of increasing throughput on delayed coking units. One refinery regularly runs 12 hour drum cycles and has attempted 10 and 11 hour cycles, but cycles this short are extremely difficult due to minimum time requirements for each of the steps of the drum cycle. Some of the more important drum cycle steps are described in detail in the following sections.

Table 1. Typical Short Cycle Coking Operations

<u>Drum Cycle</u>	<u>Hours</u>
Steam to Fractionator	0.5
Steam to Blow Down	0.5
Depressure, Water Quench and Fill	4.5
Drain	2.0
Unhead Top and Bottom	0.5
Cutting Coke	3.0
Rehead / Steam Test / Purge	1.0
Drum Warm-Up (Vapor Heat)	4.0
<hr/>	
Total Time	16.0

Drum Warm-Up (Vapor Heat). To prepare the cold empty coke drum to be put back on-line to receive the hot feed, hot vapors from the on-line drum are circulated into the cold empty drum. The hot 415°C (780°F) vapors condense in the cold drum, heating the drum to a target temperature of around 340°C (650°F). While the drum is heating, the condensed vapors are continuously drained out of the drum.

On-line Filling. After the cold drum has been vapor heated for a few hours, hot oil from the tube furnace at about 485°C (905°F) is switched into the drum. Most of the hot vapors condense on the colder walls of the drum, and a large amount of liquid runs down the sides of the drum into a boiling turbulent pool at the bottom of the drum. The drum walls are heated up by the condensing vapors, so less and less vapors are condensing and the liquid at the bottom of the drum starts to heat up to coking temperatures. A main channel is formed similar to the trunk of a tree. As time goes on the liquid pool above the coke decreases

and the liquid turns to a more viscous type tar. This tar keeps trying to run back down the main channel which can coke at the top causing the channel to branch. So the limbs of the "tree in the drum" appear [6].

This progresses up through the coke drum. Sponge coke, which includes needle coke, is formed from this liquid which remains in a quiescent zone between the main branches or channels up through the coker. The liquid pools in the quiescent zones slowly turn to solid coke. Shot coke has a different type of coke structure indicating that it is produced while suspended in the vapor phase in the drum. This will be discussed in detail later in the paper.

On top of the liquid layer is foam or froth. Paraffinic type feedstocks with some sodium present foam readily compared to aromatic feedstocks which tend to have smaller foam heights. Higher temperatures greatly decrease the height of the foam. At high temperature, needle coke has very small or no foam present. After the coke drum is filled, the hot oil is switched to the new drum.

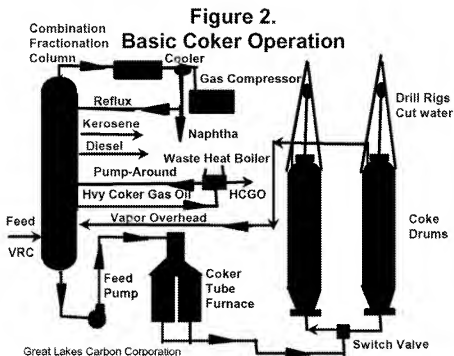
Steam-Stripping / "Hot Spots." Steam must be flowing before the switch and immediately after the switch; otherwise, the yet unconverted liquid feed on top of the coke bed will run down the channels which will coke or solidify and plug the channels. The plugging of the channels causes problems in cooling the coke since sections of the coke bed will be isolated from the steam and cooling water by the plugged channels. This is the cause for "hot spots" and "steam eruptions" when cutting the coke. Cold water from the cutting nozzle hits the exposed hot coke which results in a steam explosion. This is particularly hazardous when the pilot hole is being cut, since the drum is filled with a large quantity of hot water. A steam explosion during pilot hole cutting can cause the hot water to erupt out of the top of the drum and has caused fatalities in the past.

Steam stripping also serves to transfer heat from the hot bottom section of the coke bed to the unconverted liquid present at the top of the coke drum. Adequate steam stripping increases the amount of recovered gas oil yield while at the same time reduces the amount of volatile matter and pitch left in the top section of the coke drum. After the steam has been flowing up through the coke bed for about thirty minutes with the vapors going to the fractionator, the vapor line is vented to blowdown system. Steam is increased for a short time or in some cases water is immediately introduced at the bottom of the drum which instantly flashes to steam. The steam is backed out and the flow of cooling water is gradually increased. The top vapor temperature in the drum may increase slightly at first before cooling due to the increased flow of steam up through the coker.

Water Cooling / "Drum Bulging." The rate of cooling water injection is critical. Increasing the flow of water too rapidly can "case harden" the main channels up through the coker without cooling all of the coke radially across the coke bed. The coke has low porosity (the porosity comes from the thermal cracking) which then allows the water to flow away from the main channels in the coke drum. Porosity of delayed coke has been measured experimentally in the past by measuring water flow through cores about the size of hockey pucks cut from large chunks of needle coke from different areas of a commercial coke drum. Most of the coke cores were found to have no porosity except the coke right at the wall which had some porosity. This explains problems that have been found to occur with drums bulging during cool down. If the rate of water is too high, the high pressure causes the water to flow up the outside of the coke bed cooling the wall of the coke drum. Coke has a higher coefficient of thermal expansion than does steel (154 for coke versus 120 for steel, $\text{cm}^3/\text{cm}^3/\text{C} \times 10^{-6}$). This was measured in the transverse direction from a chunk of needle coke. The coefficient of thermal expansion for raw sponge coke is probably even greater than that of the needle coke tested.

DELAYED COKING UNIT HARDWARE

A basic coker operation flow diagram is shown below in Figure 2 to illustrate some of the delayed coking unit hardware.



Feed Preheat

In some refineries, delayed coker feed which is usually vacuum reduced crude (VRC) arrives at the coker hot, straight from the vacuum distillation unit, but in most cases, delayed coker feed is relatively cold coming from tankage. The feed is preheated by heat exchangers with gas oil products or in some rare cases by a fired coker preheater (tube furnace). In some refineries, the convection section of the main coker furnace is used to preheat the cold feed. The hot coker feed, ranging from 360 to 400°C (680 to 750°F), then enters the bottom of the fractionator / combination tower where the fresh feed is combined with some condensed product vapors (recycle) to make up the feed to the coker heater. The fractionator bottom provides some surge storage capacity for the incoming fresh feed, and in some units, heat is transferred to the fresh feed by flowing a split of the fresh feed above the drum overhead vapor entrance to the fractionator. This practice usually results in increased amounts of heavy coker gas oil recycle in the furnace charge.

Coker Charge Pumps

The coker charge pumps located between the fractionator bottom and the coker heater are normally driven by an electric motor with a steam-driven turbine pump as a backup. The pressure is in excess of 35 bars (500 psig) with a mechanical seal operating up to 382°C (720°F).

Coker Tube Furnace

The coker tube furnace is the heart of the delayed coking process. The heater furnishes all of the heat in the process. The outlet temperature of a coker furnace is typically around 500°C (930°F) with a pressure of 4 bars (60 psig).

Coker Furnace Design.

Delayed coker furnace design objectives according to Elliott [7] are:

- High in-tube velocities resulting in maximum inside heat transfer coefficient
- Minimum residence time in the furnace, especially above the cracking temperature threshold
- A constantly rising temperature gradient
- Optimum flux rate with minimum practicable maldistribution based on peripheral tube surface
- Symmetrical piping and coil arrangement within the furnace enclosure
- Multiple steam injection points for each heater pass

Normally the modern-day furnace has two to four passes per furnace. The tubes are mounted horizontally on the side and held in place with alloy hangers. The furnace tubes are around 100 mm ID with 6 to 12 mm wall thickness and are at least a 9% chrome alloy. Higher alloy tubes are being used with the more rapid steam spalling and steam-air decoking methods. Aluminized tubes have been tried, but offer no advantage. Multiple burners are along the bottom of the radiant wall opposite from the tubes and are fired vertically upward. The burners for each firebox are controlled by the temperatures of tubes in that firebox only. The control thermocouple for the firebox should be three or more tubes back from the outlet to prevent coke forming on the thermocouple. The outlet thermocouple is initially read and an off-set from the control thermocouple is then used to control the furnace. Tall furnaces are advantageous since the roof tubes are less likely to have flame impingement and overheating by both radiation and convection. Normally just the radiant section of the heater is used to heat the oil for a delayed coker. The upper convection section of the coker heater is used in some refineries to preheat the oil going to the fractionator or for other uses such as steam generation.

The typical gas burners in a delayed coker furnace are 3 MM BTU size. Adams [8] stated that the burners will produce flame height of around 0.33 meter per 1 MM BTU. Elliott [7] and others state that the average radiant flux rate should be below 9000 BTU/HR/FT² with cold oil velocity of 2 meters/sec (6 ft/sec) or mass velocity of 1800 kg/sec/meter² (400 lb/sec/ft²) or greater. Velocity steam is added at around 1 wt% of the feed. This helps increase the velocity in the tube furnace, and reduces the partial pressure in the drum so that more gas oil product is carried out of the drum. The specific heat of the steam is less than the oil, so steam is not a good source of heat in the drum. The main use for the steam is that it keeps the velocity flowing in the tube furnace if the oil flow is momentarily is lost or decreased which reduces the chance of coking up the furnace tubes.

Heater Tube Decoking. When coke forms in the heater tubes, it insulates the inside of the tube which results in elevated temperatures on the outside of the tube. With good operational practices, coker furnace run lengths of 18 months are possible before decoking of the tubes is needed. When temperatures approach 677°C (1250°F) on the exterior skin thermocouple, the furnace must be steam spalled and/or steam-air decoked or cooled down and cleaned by hydraulic pigging.

Steam Spalling. Steam spalling was probably first practiced by Exxon but was perfected by Lloyd Langseth while operating the cokers at Arco in Houston, Texas in the 1970's. He was able to operate a coker furnace over four years without shutting down by practicing on-line steam spalling. The only reason he had to shut down was that Texas had a law that required steam boilers to be inspected every five years.

On-line steam spalling requires replacing the oil with steam in the pass and then heating and cooling the tubes to snap or spall off the coke inside the tube. The steam and coke go into the drum. The main problem is in controlling the velocity and speed of spalling off the coke. Too rapid spalling can plug the tube outlet, and too high steam velocity can erode the metal in the elbows. In one refinery, return bends failed after the second steam spalling. Steam spalling requires that the delayed coker be supplied with four passes or more.

Attempts to steam spall a two-pass furnace has been tried, but the large amount of steam being handled caused problems in the fractionator.

Steam-Air Decoking and Pigging. The usual method of decoking the tubes in a coker furnace is to take the furnace off-line, steam spall, then burn the coke out of the tubes by steam-air decoking. After steam-air decoking, the tubes need to be water washed since the salts still remain in the tubes and will cause rapid coking of the tubes. A new method of decoking the tubes is to steam spall, and then use water pressure to push Styrofoam pigs with studs and grit on the exterior through the tubes and around u-bends (even u-bends with clean-out plugs). The pigs scrape out the coke without scratching the tube walls. Early methods of pigging coker heaters left scratches on the tube walls, but with the grit-coated pigs, pigging just polishes the inside of the tube wall. Pigging is faster than steam-air decoking, and refiners generally have longer campaigns on the heater compared to steam-air decoking.

Heater Tube Deposits. Iron sulfide is probably not totally removed in steam-air decoking. Coke deposits have very high content of iron, silica and sodium. Deposits recovered from return bend clean-out plugs are sometimes long cylindrical shapes and in another case looked like a thick scallop shell. These deposits were mostly sodium and calcium.

Transfer Line and Switch Valve

Transfer Line. The line from the furnace to the switch valve and on to the drum is referred to as the transfer line. The transfer line must be very well insulated to prevent coking and plugging. The shorter the line the better. Long transfer lines with many crosses and tee's used for clean outs will rapidly coke and increase the pressure on the furnace which usually results in increased fouling of the tubes in the furnace.

Flanges near the drums are difficult to insulate without causing the joints to leak. Some transfer lines have a pressure relief valve in the line, but most furnaces and transfer lines are designed to withstand the maximum pressure the charge pump can produce in case of an accidental switch into a blinded valve.

Switch Valve. The switch valve is a three-way valve with ports to the two drums and a port (recirculation line) back to the fractionator which is used in startup and shutdown. Older cokers used a manually operated Wilson-Snyder valve which was a tapered plug valve that required unseating before rotation. The newer units and retrofits are using ball valves which are usually motorized. One problem with the ball valves is that many separate steam purge lines are required to keep coke from forming on the seal bellows. If the steam purges are not monitored they can decrease the temperature of the oil going to the coke drum resulting in high volatile matter coke being produced.

Coke Drums

The coke drum diameters range from 4 to 9 meters (13 to 30 ft) with the straight side being around 25 meters (82 ft) with a 1.5 meter diameter top blind flange closure and a two meter diameter bottom blind flange in which the 15 to 30 cm diameter inlet nozzle is attached. Both the top blind flange and the bottom must be removed when decoking the drum. Usually the drum is constructed from 25 mm of carbon steel and is clad internally with 2.8 mm of stainless steel for protection against sulfur corrosion. The pressure ranges from 1 to 5.9 bars, typically around 2 to 3 bars. The vapor outlet nozzles, 30 to 60 cm diameter, are located at the top of the drum. Pressure relief valves are also located on the top of the drum on modern cokers. The outside of the drum is insulated with around 10 cm (4 in.) of fiberglass insulation with an aluminum or stainless steel covering. The coke level in the drum is usually determined with three nuclear backscatter devices mounted on the outside of the drum.

Overhead Vapor Lines

The vapor overhead line runs from the top of the coke drum to the fractionator. The temperature in the line is around 443°C (830°F). The temperature is decreased by about 28°C (50°F) by injecting hot heavy coker gas oil into the line as quench oil. This prevents coking in the line. The heavy coker gas oil is a wash oil coating the inside of the pipe. If the liquid layer dries out, coke starts to form. Some refineries leave the insulation off the overhead lines to help drop the temperature and keep the inside wetted. Prevention of coke in the line is important since this will increase the pressure in the coke drum thus increasing reflux of gas oil in the drum. Decreasing coke drum pressure increases liquid yield (decreases coke yield). Also, high pressure drops in overhead lines can cause foaming in the coke drum during the drum switch. Vapor line sizes are very large in order to obtain the minimum amount of pressure drop. One refinery used two 760 mm (30 inch) vapor lines in parallel.

Antifoam Injection System

Injection of silicon antifoam should always be furthest away from the vapor overhead line outlet at the top of the drum to prevent silicon from being carried overhead into the vapor lines to the fractionator. The heaviest possible antifoam that can be handled in the refinery should be used. Lower viscosity antifoams appear to break down at lower temperatures and are not as effective. Usually a carrier stream is used to carry the antifoam into the drum, heavier carrier material would not be as easily flashed off in the drum. Several refineries are using less antifoam and having less problems with foam since starting continuous injection of antifoam. A Dow Chemical Company representative stated in 1981 that it is easier to prevent a foam than it is to kill a foam. Also, when a foam is broken down, it still leaves a mist which can cause coking in the bottom of the fractionator. A rule of thumb is that antifoam should cost around \$0.10 per ton of coke produced. Costs different than this may indicate that too much or too little antifoam is being used.

Coker Fractionator

The fractionator or combination distillation tower separates the coker overheads into gases, gasoline, diesel, heavy coker gas oil (HCGO), and recycle. An oversized fractionator can be used to maximize the amount of diesel product and minimize the heavy coker gas oil to the FCCU. Hot overhead vapors can cause coking in the lower section of the fractionator if trays are not kept washed (wet). The major amount of heat is removed in the heavy coker gas oil section by trapping out the oil and then extracting the heat with heat

exchangers or steam boilers. This pump-around HCGO is then pumped back into the tray above the trap-out tray. Some of the HCGO is sprayed below the trap-out tray to wash and cool the hot vapors. Trap-out trays can be used to catch some of this oil and reduce the amount of recycle oil going back to the furnace. Packing can be used in fractionators to reduce the pressure drop, but it is critical to keep the packing wet to prevent coking in the packing. The pressure in the fractionator and also the coke drums is controlled by the gas compressor at the top of the fractionator.

The fresh feed from the vacuum distillation (VRC) should go directly to the bottom of the tower since the effective temperature of distillation is higher than in the fractionator. Originally when some cokers were designed to coke atmospheric reduced crude, the feed was sprayed into the fractionator above the vapor inlet to fractionate out more light ends in the feed. If VRC is injected above the vapor it condenses out part of the HCGO into the bottom of the fractionator increasing the recycle to the coker furnace. The bottom of the fractionator should be operated at as high a temperature as possible without causing coking in the bottom in order to keep the tube furnace duty low. Normally the temperature in the bottom ranges from 343°C (650°F) to 382°C (720°F) without coke formation in the bottom of the fractionator. A slotted stand pipe in the bottom of the fractionator feeds the furnace charge pump.

Hydraulic Coke Cutting System

Cut Water Pump. High pressure water is used to cut the coke out of the drum. Water pressures range from 86 bars (1250 psig) to 275 bars (4000 psig) and flow rates range from 2.8 cubic meters per minute (750 GPM) to 4.7 cubic meters per minute (1250 GPM). Cut water pumps are multistage barrel type or split case multistage pumps which were originally developed for feed water pumps for steam boilers. The pumps are usually powered with an electric motor, but some older units use steam-driven turbines.

Cutting Equipment. Derricks are built on top of the drum so that the drill stem (5 to 6 inch extra heavy pipe) can be moved with a winch and cable. The high pressure water flows through an API 10,000 psi drilling hose to the top of the drill stem. The drill stem is rotated with an air motor at the top through a rotary joint. The cutting nozzles are the pilot bit with down facing nozzles and the cutting bit with nozzles facing outward. New units have both nozzles incorporated into a single drilling head.

Coke Cutting Technique. A pilot hole approximately one meter in diameter is drilled from the top of the drum to the bottom. The pilot hole must be cut down through the coke with minimum weight on the bit, since if pushed, the bit can follow the main channel in the coke drum, bend, and stick the drill stem in the coke. After completing the pilot hole, the pilot bit is changed to the cutting bit, and the bottom of the hole is belled out and opened up to around two meters in diameter to prevent plugging. The bit is then pulled to the top of the drum and cutting begins by spiraling downward at four to six RPM with vertical movement of one-half meter per revolution of the drill stem. Usually a vertical four meter section will be cut by moving the drill stem up and down until the coke is all cut out of the section. Normally around 15 to 20 minutes are required to drill out the pilot hole and three to four hours to cut the coke. The coke can be cut directly into rail cars, cut into a crusher car and the coke pumped hydraulically, or cut into a pit or pad with cranes or end loaders moving the coke.

COKE FORMATION, PROPERTIES, AND STRUCTURE

Crude Oil Origin

In order to understand the components of petroleum coke, we must review the origin of the vacuum reduced crude (coker feed) and crude oil from which it originates. The formation of crude oil is thought to be derived from ancient remains of animals and plants. The organic matter was squeezed out of the strata probably by the connate water or water that was originally in formation. Ancient stream beds, reefs, and sand beaches had the porosity to allow migration of the oil water and provided a conduit for this oil and water material to flow. The final requirement is a trap for the oil. Oil is not in an open pool but is trapped between layers of sand or in cracks of limestone. The basic trap is the anticline where the formations were pushed up into a dome shaped area where the oil and gas accumulated. Also, faulting of geologic formations pushed oil up against some impervious formations forming fault traps. The salt domes in the Gulf Coast of the United States have been big producers of oil. Spindletop near Beaumont, Texas was a prime example. Salt laid down in the bottom of a drying sea, and these formations were covered by over five miles of sediment. The resultant pressure liquefied the salt which then started to migrate toward the surface. The geologic formations are pushed up as the salt plug punches through the formations. The salt, being impervious to the oil, forms an excellent trap.

The vanadium and nickel are in the crude oil as porphyrins or metal chelates. Originally the metals were probably magnesium (chlorophyll) and iron (hemoglobin). The ratio of the metals to each other is due to when and how they were buried. Some of the vanadium and nickel can be loosely held between the asphaltene molecules (intercalation). The other metals are complexed onto the water droplets and probably were due to the structure that the oil migrated through. Crude oils such as the Paraffinic Pennsylvanian crude contain very small amounts of asphaltenes. It is possible that the asphaltenes dropped out of the oil phase but are still down in the formation.

Parts of Crude Oil

Crude oil contains three different fractions. The "Oil" is the hydrocarbon: paraffinic, naphthenic, and aromatic which also contain sulfur and nitrogen. The second part of the crude oil, the resins, coat the asphaltene fraction so that it can be peptized into the crude oil. The resins are a brown, sticky hydrocarbon which contain nitrogen, oxygen, and sulfur, are soluble in n-pentane but insoluble in propane, and have molecular weights greater than 3000. The asphaltenes contain the chelated metals, vanadium, nickel, and possibly some calcium along with sulfur, oxygen, and nitrogen. During crude oil distillation, the asphaltenes are not volatilized and remain in the vacuum reduced crude along with most of the resin fraction. Jakob [2] thought that all the resins and asphaltenes dropped out in the coker and the remaining coke was made from the oil fraction. With higher temperatures and lower pressures, the hydrocarbon part of the coke could be reduced but not the resin and asphaltene fraction. The amount of coke produced in a delayed coker is always more than the Conradson or Ramsbottom carbon residue percentage by a factor of about 1.6.

Desalter's Influence on Coke Properties

The crude oil desalter is one of the most critical pieces of equipment in the refinery for producing good quality anode grade coke (coke low in metals suitable for calcination and use in the aluminum industry) and keeping a coker furnace on line. Crude oil contains around 0.2% water in which is mixed the soluble salts

such as sodium chloride and other metals which are on the edge of the sphere of water. In desalting, the crude oil is washed with 5% water to remove the salts and dirt from the crude oil. The water, being heavier than oil, drops out of the bottom, and the cleaned oil flows overhead with around 0.1% water.

Without good desalting, caustic (sodium hydroxide) or filming amines must be added to eliminate the chloride corrosion in the overheads of the distillation and vacuum distillation lines. The chlorides are usually in the form of salt (sodium, calcium, and magnesium chloride) The salt content can vary from 50 to 300 lbs per 1000 barrels of crude. Since the number of droplets are high, around 9×10^{11} , the amount of dirt and other metals on the outside of these water droplets is appreciable. The magnesium chloride causes most of the corrosion since it breaks down at low temperatures in the distillation column liberating chlorine which forms hydrochloric acid that attacks the overhead lines in both the vacuum and atmospheric distillation units.

Sodium is a catalyst for burning of carbon (air and carboxyl reactivity in baked anodes) and also causes rapid fouling in the coker tube furnace. The mechanism for rapid fouling of tubes due to sodium is not fully understood, but it is known that if the tubes are not water washed after steam-air decoking to remove the crystals of salt, the unit will rapidly foul. Iron in fine particles, probably iron sulfide, is very difficult to remove in a desalter, but some chemical companies can do a better job than others. Metals that the desalter does not remove will end up in the coker feed and ultimately in the delayed coke.

Coke Physical Structure

Coefficient of Thermal Expansion. To determine a quantitative value describing coke structure, the coke is calcined, ground to a flour, mixed with coal tar pitch, extruded to orientate particles into 13 mm rods, baked to 850°C, and graphitized to 2900°C, and then the difference in expansion at 0°C and 50°C is measured for Coefficient of Thermal Expansion (CTE) determination. Typical values of CTE corresponding to coke structure are: needle coke (acicular), 0 to 4; sponge coke, 8 to 18; and shot coke (isotropic), > 20 (cm/cm°C $\times 10^{-7}$).

Shot Coke. The production of shot coke in a delayed coker requires high concentrations of asphaltenes in the feedstock, dynamics (velocity and/or turbulence) in the coke drum, and high coke drum temperatures. A coker feedstock high in oxygen content can also produce shot coke. When asphaltene content compared to the Conradson carbon residue content of the coker feed is high, the production of shot coke is very likely. The present trend in refineries is to run heavier crudes with higher asphaltene contents and to improve operation of the vacuum distillation unit to produce a heavier VRC with a higher asphaltene content. This trend toward increased production of shot coke has been observed in refineries which originally ran atmospheric reduced crude in the delayed coker, never making shot coke, that started producing shot coke after a vacuum distillation unit was installed.

Shot coke is produced as the oil flows into the coke drum. With the light ends flashing off, small globules of heavy tar are suspended in the flow. These tar balls rapidly coke due to the exothermic heat produced by asphaltene polymerization. (Cokers going from sponge coke production to shot coke production have seen the drum overhead temperature increase by as much as 3°C.) The balls then fall back into the drum as discrete little spheres two to five millimeters in size. In the main channel up through the drum, some of the spheres will roll around and stick together forming large balls as large as 25 centimeters.

When these large balls are broken, they are found to be composed of many of the two to five millimeter size balls. Normally, small shot coke balls from different delayed cokers will be nearly the same size; however,

Mexican Mayan VRC has been found to produce larger shot coke balls upon delayed coking than does Venezuelan VRC. It is thought that smaller balls are made when very high feed rates are used in the coker. Aromatic feeds, such as decant oil from the FCCU, can help eliminate shot coke formation. All other methods of eliminating shot coke such as decreasing temperature, increasing drum pressure, and increasing recycle ratio, will all increase coke yield (decrease more valuable liquid yields) which is not desired.

It is very difficult to produce shot coke spheres in a pilot delayed coker. Spherical shot coke can only be produced in pilot delayed cokers if the velocity in the drum and the temperature in the drum are both very high. In a batch (pot) coker, the typical spherical form of shot coke cannot be produced at all; but the shot coke micro-structure in the batch-produced coke can be seen with a microscope, and the batch-produced coke does have a high CTE value similar to the spherical form.

Shot coke is unique in that the small spheres two to five millimeters in diameter each have a slick shiny exterior coating of needle or acicular type carbon. The inside of each sphere contains isotropic or amorphous type coke as originally described by Marsh and Bacha [10]. Shot coke cannot be used in making aluminum anodes because the outer needle coke layer of the shot sphere has a very low coefficient of thermal expansion while the inside of the sphere, being isotropic, has a very high coefficient of thermal expansion.

When rapidly heated in a calcining kiln, the outer layer is cracked and pulled away from the center; thus when used in an anode with a coal tar binder, the binder adheres to the outer layer (egg shell). This results in many cracks between the ball and the skin causing the anode to crack and dust in an aluminum smelter cell [11].

Sponge Coke. Sponge coke is named for its sponge-like appearance and is produced from VRC with a low to moderate asphaltene concentration. If sponge coke meets strict property specifications, it is considered anode grade sponge coke suitable for calcination for use in making carbon anodes for the aluminum industry. Otherwise, if sponge coke meets the more lenient fuel grade specifications, it can be used in its raw form for fuel.

The biggest problem for refineries producing anode grade sponge coke is obtaining the low volatile matter (VM) required. The metals and sulfur are strictly controlled by the crudes being processed, but the VM is in the control of the delayed coker operators. Temperature in the drum is the most critical item, along with cycle time and drum pressure. Longer residence time at temperature helps to decrease the VM. Increased recycle can increase the temperature in the drum. Insulation of the transfer line and coke drum, especially the upper sections of the coke drum, are critical for obtaining low VM coke. Poor insulation and other bad practices on the delayed coker require higher temperatures in the tube furnace, which results in shorter campaigns and more downtime for decoking of the furnace. Monitoring the seal steam to prevent decreasing the temperature in the transfer line, elimination of seal oil on the pressure relief devices on the transfer line, and minimizing the amount of carrier oil for the antifoam all help in increasing the temperature in the drum in order to decrease VM of the resultant coke.

Raw or "green" sponge coke must be calcined before it can be used in making anodes. The density of the calcined coke is critical for producing good carbon anodes. The higher the density, the more carbon can be incorporated into the anode, and the longer the anode will last. Vibrated bulk density (VBD) of the calcined coke must be greater than 86 (grams/100 cc). The best single property that correlates from the raw coke is the Hardgrove Grindability Index (HGI). Raw coke with lower than 70 HGI usually can be calcined to produce an 86 VBD. Volatile matter is another good property used to correlate how well the raw coke

will calcine. Structure is a strong factor in calcinability also, since cokes with low CTE must have volatile matter much lower than a more isotropic type coke to produce the same density. Porosity of the calcined coke should be low and is also a function of the raw coke volatile matter. The ash in the calcined coke is normally around 0.2 % with vanadium and nickel combination under 500 ppm. Sodium and calcium are very strong catalysts for air burn of an anode. Vanadium, nickel and iron and other metals causes increased carboxyl reaction in the bottom of the anode. The sulfur in the anode must be below 3.5% to prevent the sulfur from increasing the electrical resistance of the cast iron connection between the anode and the power rod. Normally, sulfur is more of an environmental and scrubbing problem. Sulfur can cause the real density of calcined coke to decrease due to an increase of the porosity and micro cracking of the calcined coke. Sulfur does help reduce reactivity (air and carboxyl) by reacting with the caustics which are strong catalysts.

Aluminum production requires around one-half kilogram of carbon per kilogram of aluminum produced. Anode grade coke must be low in metals concentration since the exhaust from the aluminum cell is being scrubbed with the alumina used as feed to the aluminum cells. Therefore, any metals in the coke would get into the alumina and into the aluminum metal produced. The carbon is used in the aluminum smelter as a means of carrying electrical power into the cell. It takes around 15 KW of power per kg of aluminum produced. A carbon with some porosity must be used since gases coming off the cell would block the power going into the cell if the anode was not porous. The high temperature along with the very corrosive fluoride salts used in the aluminum cell and the problem with the evolution of the gases makes the discovery of a non-consumable anode difficult.

Needle Coke. Needle coke, named for its needle-like structure, is produced from feedstocks without asphaltenes present, normally FCCU decant oils. Needle coke is the premier coke, used in graphite electrode manufacturing (used in steel arc furnaces) and commands a high price (calcined ultra-premium non-puffing, \$500 per ton); but needle coke requires special feedstocks, special coking, and special calcination to obtain the optimum properties that it requires. The Shea patent on needle coke [12] gives an accurate description of the formation of needle coke, still relevant today. Most needle coke is produced from hydrodesulfurized decant oil (due to the low sulfur requirement for non-puffing coke, that can be nearly flash graphitized in the new direct current (DC) length-wise graphitization method, without splitting the electrode). The principle requirement for needle coke is that the CTE must be 2.0 or below (low CTE is required to prevent spalling due to the thermal stresses on the tip of the electrode which can be as high as 2000°C/cm). Needle coke must have low sulfur (<0.6 wt%) and nitrogen contents in order to be non-puffing during graphitization to 2900°C (measured by a special dynamic puffing test that is proprietary). Needle coke must also have a maximum amount of coarse sizing (>6 mm), a minimum amount of fines (<1 mm), good density (>78 grams/100 cc; 4/6 mesh test), low ash content (<0.3%; any ash leaves a void when graphitized), and a high real density (2.13 grams/cc).

Even with all the property specifications, an electrode manufacturer will not accept a calcined needle coke for production until they have actually run a trial lot through the plant and trials on the electric arc furnace. Most graphite plants want a needle coke with low variability so that they can set up the optimum pitch level, extruding and baking to produce a good electrode. The most popular electrode is the 24 inch (60 cm), with a demand for larger than 30 inch (76 cm) for DC single electrode furnaces. Obtaining good needle coke is still a "black art" for excellent graphite electrodes. The principal property that the electric arc steel mill wants in a graphite electrode is a low amount of graphite per ton of steel melted. In single electrode DC furnaces, the amount of graphite per ton is below 2 kg/ton. With better practices and foamy slag, AC furnaces (using three electrodes due to three-phase electric power) have approached this level.

Pilot Delayed Coker and Coke Formation Model

In the 1970's, Great Lakes Carbon obtained a design for a pilot delayed coker and modified and improved the design to produce needle coke identical to that which is commercially produced. Non-puffing needle coke was in short supply at that time with prices for raw coke running over \$600 per short ton. The pilot unit had a 305 mm (12 in) diameter drum 2.13 meters (84 in) tall, a gas fired tube furnace (both convection and radiant sections), self-generated recycle (up to 400%), an operating pressure of up to 6.8 bars (100 psig), adiabatic drum conditions, load cells on feed tanks, overhead receivers, gas meters, and a Ranarex (for determining molecular weight of overhead gases). A very good material balance could be obtained.

The unit produced around 70 kg (>150 lbs) of coke which was calcined in a gas fired pilot calciner. The coke drum was decoked by cutting the head off the drum with a metal band saw and then trepanning the coke out with a large core drill.

Due to the extreme hardness of needle coke, the specified auger type cutter could not be used for decoking and a core bit was designed and built. By using the core bit, the coke came out in long sections which could then be sliced with a band saw. From studying these slices of coke, GLC discovered how coke forms in the drum. This discovery was confirmed by sampling many railcars of commercially produced needle coke and observing a puzzling strange-looking coke found on the very large piece cut from the lower section of the drum near the knuckle. This coke was typical except the center contained a dull looking, very friable coke. Also, looking up at the bottom of the coke bed after the bottom blind flange was removed on a delayed coker, a hole was observed going up in the bottom of the coke drum. From these observations of commercial delayed coke and from studying the slices from the pilot unit, the "tree in the drum" channel branching theory was formulated. This coke formation model is illustrated in Figure 3 shown below [6,13].

Figure 3. Great Lakes Carbon Coke Formation Model: How Coke Forms in the Drum

Structure Orientation In Drum. Samples of coke cut both vertically and horizontally showed that the coke was oriented in the drum. The coefficient of thermal expansion is much lower in the vertical direction compared to horizontal, 132% lower in the raw coke, 505% lower in the calcined, and 2850% lower in the graphitized sample (see Table 2). Gas bubbles, formed from cracking, migrate upward during coke formation in the liquid, orientating the mesophase chain growth.

Table 2. Coke CTE by Orientation

CTE (cm/cm/°C x 10 ⁻⁷)	<u>Vertical</u>	<u>Horizontal</u>
Raw Coke	117	154
Calcined 850°C	1.8	9.1
Graphitized 2900°C	0.2	5.7

[13]

Chemical Property Distributions. The ash is mainly in the lower sections of the coke drum with a high percentage in and near the channels up through the coker. The ash being a particulate drops out of the oil, or the wall of the channel traps out the particle, otherwise known as the "fly paper effect." A cross-section of the coke in the drum was cut into small cubes which were analyzed for ash content. The ash

level was five to ten fold higher near the channels compared to the rest of the section. In an experiment where a paint pigment sized chromium oxide was pumped through the tube furnace into the coke drum in an attempt to get good dispersion in the coke (chromium oxide is a puffing inhibitor in needle coke), all the chromium oxide dropped out in one spot in the lower section of the coke drum up about six inches from the inlet. This is normally the first spot where the main channel starts to branch. Several runs were made with identical results. Injecting the pigment through the top of the drum distributed the material uniformly in the coke, indicating that there is some back mixing in the top of the drum either in the froth layer or in the liquid.

Iron, silicon, and ash are in the coke as particulates. These metals concentrate in the lower section of the coke drum as shown in Table 3 below. Vanadium and nickel are in crude oil as metal chelates or porphyrins in the asphaltene fraction. It was puzzling that vanadium and nickel are not uniformly distributed in the drum until it was understood that some of the metals are intercalated in the structure and are not chemically bonded, so they drop out early in the coke drum similar to the ash and particulates. Volatile matter (VM) in the coke drum is normally high in the top of the drum due to the short residence time of the material. The sulfur is uniformly distributed in the drum unless the feedstock to the drum is changing as the drum is filled [13].

Table 3. Property Distributions in the Coke Drum (wppm)

	<u>Top</u>	<u>Middle</u>	<u>Bottom</u>
Iron	40	440	1300
Silicon	60	150	380
Ash	1000	2100	4500
Vanadium	267	310	380
Nickel	130	160	230
VM (wt%)	11.8	9.5	9.4

[13]

USES OF PETROLEUM COKE

Raw Petroleum Coke

Fuel Coke. Fuel grade coke (shot or sponge) is used in the production of cement and with fluidized bed boilers (using limestone for sulfur removal) for generation of steam and electricity. The important properties for pulverized fuel coke is the cost per BTU, high HGI, and sulfur content. Vanadium in petroleum coke does not cause corrosion on boiler tubes as does vanadium in heavy fuel oil.

Metallurgy Uses. Some raw petroleum coke, if the sulfur is low enough, can be blended into feed for slot ovens which produce blast furnace coke. Petroleum coke increases the physical strength and density of the coke when blended with coal.

Gasification. Partial oxidation of petroleum coke in a gasification process enables raw petroleum coke to be used to produce steam, electricity, or gas feedstocks for the petrochemicals industry.

Calcined Petroleum Coke - Other Uses

Some calcined petroleum coke is used in production of titanium dioxide (in the chloride process), production of carbon monoxide for production of plastics, as a feedstock for continuous particle thermal desulfurization for special low sulfur carbon raiser (steel ladle additive), or as carbon raiser in cast iron and steel making.

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